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**Title of the Invention: Stabilized Flame-Retardant  
Thermoplastic Resin Composition**

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**(54) Title of the Invention: Stabilized Flame-Retardant Thermoplastic Resin Composition**

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**SPECIFICATION**

**1. Title of the Invention**

**Stabilized Flame-retardant Thermoplastic Resin Composition**

**2. Claims**

A stabilized flame-retardant thermoplastic resin composition obtained as a result of adding a halogenated phosphate ester and a  $\beta$ -diketone compound to a thermoplastic resin.

**3. Detailed Description of the Invention**

The present invention relates to a stabilized flame-retardant thermoplastic resin composition.

More specifically, it relates to a stabilized flame-retardant thermoplastic resin composition obtained as a result of adding a halogenated phosphate ester and a  $\beta$ -diketone compound to a thermoplastic resin.

Thermoplastic resins such as polyethylene, polypropylene, polyester, polyvinyl chloride, and polymethacrylate have excellent properties such as electrical properties, water resistance, and chemical resistance and have been widely used in recent years in electrical insulating materials, construction materials, clothing, sundry goods, and the like. These resins, however, generally have carbon, hydrogen, and/or oxygen as the main structural components. They have no resistance to ignition and, when ignited, spread the fire easily and produce large amounts of smoke. This ignitability and combustibility of thermoplastic resins greatly limit their use from the viewpoint of preventing fires and protecting people.

To improve upon this drawback, the use of various flame retardants has been proposed to impart flame-retardancy to thermoplastic resins and to make them self-extinguishing. Examples of compounds that can be used singly or in combinations include chlorinated paraffin, chlorinated polyethylene, pentachlorophenol, perchlorocyclopentadecane, tetrabromoethane, tetrabromobutane, hexabromocyclododecane, and other such halides; tricresyl phosphate, cresyl phosphate, trimethyl phosphate, tributyl phosphate, trioctyl phosphate, tributoxyethyl phosphate, triphenyl phosphate, and other such phosphate esters; tris(chloroethyl)phosphate, tris(2-chloropropyl)phosphate, tris(2,3-dibromopropyl)phosphate, tris(bromochloropropyl)phosphate, 2,3-dichloropropyl-2,3-dichloropropyl phosphate, and other such halogenated phosphate esters; and antimony trioxide, barium metaborate, aluminum hydroxide, barium hydroxide, and other such inorganic compounds.

However, compounds that contain halogens readily undergo dehydrohalogenation due to light and heat. This markedly lowers the properties by causing discoloration, coloration, degradation, and other undesirable changes in the resin during molding. Also, the gas produced as a result of the decomposition not only corrodes the processing machinery and other equipment, but also is toxic to the workers. The use of phosphate esters is greatly limited on account of their high volatility and hydrolyzability. A relatively large amount also must generally

be added in order to be able to expect an adequate flame-retarding effect, and this markedly lowers the properties of the resin.

As a result of extensive research undertaken by the present inventors in light of this situation, they discovered a flame-retardant thermoplastic resin composition with excellent heat stability, water resistance, weather (light) resistance, and physical properties and thereby attained the present invention.

Specifically, the present invention provides a stabilized flame-retardant thermoplastic resin composition obtained as a result of adding a halogenated phosphate ester and a  $\beta$ -diketone compound to a thermoplastic resin.

The present invention will be explained in detail below. Examples of the halogenated phosphate ester in the present invention include tris(2-chloroethyl)phosphate, tris(2-bromoethyl)-phosphate, tris(dichloropropyl)phosphate, tris(chloropropyl)phosphate, tris(bromopropyl)-phosphate, tris(2,3-dibromopropyl)phosphate, tris(bromochloropropyl)phosphate, bis(chloropropyl)monoocetyl phosphate, bis(bromopropyl)monoocetyl phosphate, bis(chloroethyl)monophenyl phosphate, bis(chloropropyl)monophenyl phosphate, bis(bromopropyl)monodecyl phosphate, bis(bromopropyl)monophenyl phosphate, bis(dichloropropyl)monoocetyl phosphate, bis(dibromopropyl)monophenyl phosphate, bis(bromochloropropyl)monostearyl phosphate, mono(dibromopropyl)bisoctyl phosphate, bis(2,3-dibromopropyl)-2,3-dichloropropyl phosphate, and bis(chloroethyl)monophenyl phosphate. Condensation products (polyphosphates) of these ester compounds can also be used. Examples include Phosguard C-22 (Monsanto), Phosguard C-22-R (Monsanto), Phosguard B-20 (Monsanto), Phosguard B-52-R (Monsanto), Phosguard 2XC-20 (Monsanto), and CR-505 (Daihachi Chemical Industry). Although the amount in which this ester compound is used is not subject to particular limitation, 5-100 parts by weight can be used appropriately per 100 parts by weight of resin.

These halogenated phosphate esters can be used in combination with other inorganic flame retardants. Examples of these flame retardants include hydrated alumina, hydrated tin oxide, ammonium bromide, antimony oxide, barium metaborate, phosphate borate, zinc borate, antimony zinc polyalkyl phosphate, boron zinc polyalkyl phosphate, sodium antimonate, zinc borate [sic], barium metaborate, zirconium hydroxide, antimony trichloride, ammonium

polyphosphate, zirconium oxide, tin oxide, and titanium phosphate. The amount added is 0.01-30 parts by weight per 100 parts by weight of resin.

Examples of the  $\beta$ -diketone compound include dehydroacetic acid, dehydropropionyl acetic acid, dehydrobenzoyl acetic acid, cyclohexane-1,3-dione, dimedone, 2,2'-methylenebis-cyclohexane-1,3-dione, 2-benzylcyclohexane-1,3-dione, acetyl tetralone, palmitoyl tetralone, stearoyl tetralone, benzoyl tetralone, 2-acetyl cyclohexanone, 2-benzoyl cyclohexanone, 2-acetyl-cyclohexane-1,3-dione, benzoyl-p-chlorobenzoyl methane, bis(4-methylbenzoyl)-methane, bis(2-hydroxybenzoyl)methane, benzoyl acetyl methane, tribenzoyl methane, diacetyl benzoyl methane, stearoyl benzoyl methane, palmitoyl benzoyl methane, lauroyl benzoyl methane, dibenzoyl methane, 4-methoxybenzoyl benzoyl methane, bis(4-methoxybenzoyl)-methane, bis(4-chlorobenzoyl)methane, bis(3,4-methylenedioxybenzoyl)methane, benzoyl acetyl octyl methane, benzoyl acetyl phenyl methane, stearoyl 4-methoxybenzoyl methane, bis(4-t-butylbenzoyl)methane, benzoyl acetyl ethyl methane, benzoyl trifluoro acetyl methane, diacetyl methane, butanoyl acetyl methane, heptanoyl acetyl methane, triacetyl methane, stearoyl acetyl methane, palmitoyl acetyl methane, lauroyl acetyl methane, benzoyl formyl methane, acetyl formyl methyl methane, benzoyl phenyl acetyl methane, bis(cyclohexanoyl)methane, and dipivaloyl methane.

The  $\beta$ -diketone compounds in the present invention also include metals salts (or complex salts) of these compounds. Examples of such metals include Group I, II, III, IV, V, and VIII metals. Metals such as lithium, sodium, potassium, magnesium, calcium, strontium, barium, and zinc are especially preferred.

The amount of  $\beta$ -diketone or metal salt (complex) used can be an arbitrary amount up to 10 parts by weight, preferably 0.0001-5 parts by weight, per 100 parts by weight of resin.

The performance can also be improved as a result of using known compounds in the composition of the present invention. These are metal salt compounds of organic acids or phenols, mercaptide compounds, organotin compounds, epoxy compounds, and organic phosphite compounds. A range of 0.01-10 parts by weight per 100 parts by weight of resin can be used.

The following compounds can also be used in accordance with the intended applications: ester-based, polyester-based, phosphate ester-based, and chlorine-based plasticizers; phenol-based and sulfur-based antioxidants; and benzophenone-based, benzotriazole-based, salicylate-based, substituted acrylonitrile-based, triazine-based, piperidine-based, and metal chelate-based photostabilizers.

The following compounds can also be included as needed: crosslinking agents, pigments fillers, foaming agents, antistatic agents, antifogging agents, bleed-out inhibitors, surface treatment agents, lubricants, fluorescent whiteners, preservatives, bactericides, metal inactivators, photodeterioration inhibitors, processing auxiliaries, mold-release agents, and reinforcing agents.

Examples of the synthetic resin used in the present invention include polyethylene, polypropylene, polybutene, poly-3-methyl butene, and other such a-olefin polymers; ethylene-vinyl acetate copolymers, ethylene-propylene copolymers, and other such polyolefins and copolymers thereof; polyvinyl chloride, polyvinyl bromide, polyvinyl fluoride, polyvinylidene chloride, chlorinated polyethylene, chlorinated polypropylene, polyvinylidene fluoride, brominated polyethylene, chlorinated rubber, vinyl chloride-vinyl acetate copolymers, vinyl chloride-ethylene copolymers, vinyl chloride-propylene copolymers, vinyl chloride-styrene copolymers, vinyl chloride-isobutylene copolymers, vinyl chloride-vinylidene chloride copolymers, vinyl chloride-styrene-maleic anhydride ternary copolymers, vinyl chloride-styrene-acrylonitrile copolymers, vinyl chloride-butadiene copolymers, vinyl chloride-isoprene copolymers, vinyl chloride-chlorinated propylene copolymers, vinyl chloride-vinylidene chloride-vinyl acetate ternary copolymers, vinyl chloride-acrylic ester copolymers, vinyl chloride-maleic ester copolymers, vinyl chloride-methacrylic ester copolymers, vinyl chloride-acrylonitrile copolymers, internally plasticized polyvinyl chloride, and other such halogen-containing synthetic resins; polystyrene; polyvinyl acetate; acrylic resin; copolymers of styrene and other monomers (such as maleic anhydride, butadiene, and acrylonitrile); acrylonitrile-butadiene-styrene copolymers; acrylic ester-butadiene-styrene copolymers; and methacrylic ester-butadiene-styrene copolymers, polymethyl methacrylate, and other such methacrylate resins, as well as polyvinyl alcohol, polyvinyl formal, polyvinyl butyral, linear polyester, polyamide, polycarbonate, polyacetal, polyurethane, fibrin resin, phenol resin, urea resin,

melamine resin, epoxy resin, unsaturated polyester resin, and silicone resin. Isoprene rubber, butadiene rubber, acrylonitrile-butadiene copolymer rubber, styrene-butadiene copolymer rubber, and other such rubbers and blends of these with resins are also acceptable.

Additional examples include crosslinked synthetic resins such as crosslinked polyethylene that has been crosslinked with a peroxide or radiation, and foamed synthetic resins such as foamed polyurethane and foamed polystyrene that have been foamed with a foaming agent.

The present invention is explained in greater detail below through working examples. It is apparent that these are intended only as examples and do not in any way limit the scope of the present invention.

### **Working Example 1**

The following mixture was kneaded for 10 minutes at a roll temperature of 125°C, and a sheet was produced. It was pressed for 5 minutes at 135°C under 250 kg/cm<sup>2</sup>, and test pieces 3.0 and 1.0 mm thick were produced. Thermal discoloration tests at 200°C (1 mm thickness) and a combustion test (3 mm thickness) based on the oxygen index (IO) method were carried out using these test pieces. The results obtained are shown in Table 1.

#### **<Mixture>**

Polystyrene resin (Diarex HT-88)	100 parts by weight
Tris(dibromopropyl)phosphate	4.0
Antimony trioxide	2.0
OP Wax	0.3
Butyltin maleate	0.2
BHT	0.1
β-Diketone compound (Table 1)	0.005

Table 1

No.	$\beta$ -Diketone compound	Thermal discoloration* <sup>1</sup>		OI* <sup>2</sup>
		0 min	60 min	
Comparative example				
1-1	None	13	60	19.6
Working examples				
1-1	Dehydroacetic acid	9	21	21.6
1-2	Benzoyl acetyl methane	10	23	21.4
1-3	Dibenzoyl methane	9	21	21.5
1-4	Stearoyl benzoyl methane	10	24	21.9
1-5	Butanoyl acetyl methane	11	24	21.8
1-6	Benzoyl phenyl acetyl methane	11	25	21.3
1-7	Dehydroacetic acid Zn salt	9	22	22.1
1-8	Dibenzoyl methane Zn salt	8	21	22.1

\*<sup>1</sup> The yellowness was measured with a Hunter colorimeter.

\*<sup>2</sup> According to JIS K-7201.

### Working Example 2

The following mixture was mixed for 5 minutes with the help of a mixer and a compound was produced with the help of an extruder. 90 × 40 × 1 mm test pieces were then produced using an injection molding machine. These test pieces were submitted to a heat stability test in a 175°C gear oven. Furthermore, all were self-extinguishing in the combustion test (ASTM D-635). The results obtained are shown in Table 2.

#### <Mixture>

Polypropylene (Profax 6501)	100 parts by weight
Calcium stearate	0.2
Dilaurylthiodipropionate	0.2
Tris(nonylphenyl)phosphite	0.1
Tris(bromochloropropyl)phosphate	5.0
$\beta$ -Diketone compound (Table 2)	0.005

Table 2

No.	$\beta$ -Diketone compound	Thermal discoloration* <sup>1</sup>	
		0 min	72 hours
Comparative example 2-1	None	9.5	12.6
Working examples 2-1	Dehydrobenzoyl acetic acid	7.8	9.3
2-2	Benzoyl tetalone	7.8	9.6
2-3	Benzoyl acetyl methane	7.9	9.7
2-4	Dibenzoyl methane	7.6	9.5
2-5	Stearoyl benzoyl methane	7.7	9.2
2-6	Dehydroacetic acid Ba salt	7.5	9.2
2-7	Dibenzoyl methane Zn salt	7.5	9.1

**Working Example 3**

The following mixture was extruded at 200°C and processed into pellets. Test pieces were produced as a result of the injection processing of these pellets at 230°C. The oxygen index was measured according to JIS K-7201 and the degree of discoloration (yellowness measured with a Hunter colorimeter) was measured after 30 hours in a 135°C Geer oven. The results are shown in Table 3.

## &lt;Mixture&gt;

ABS resin (Styrex 200)	100 parts by weight
Calcium stearate	1.0
Trisnonylphenyl phosphite	0.3
Tris(2,3-dibromopropyl)phosphate	5.0
$\beta$ -Diketone compound (Table 3)	0.005

Table 3

No.	$\beta$ -Diketone compound	Thermal discoloration		OI
		0 hr	30 hrs	
Comparative example 3-1	None	13	58	24.2
Working examples 3-1	Dibenzoyl methane	9	14	26.1
3-2	2-Benzoyl cyclohexanone	10	18	25.7
3-3	Benzoyl acetyl ethyl methane	10	20	26.0
3-4	Palmitoyl acetyl methane	11	21	25.9
3-5	Stearoyl benzoyl methane	9	17	26.2

**Working Example 4**

The following mixture was kneaded with rolls, and 0.5 mm thick sheets were produced. The heat stability and initial discoloration were studied at 175°C. A combustion test was also conducted according to ASTM D-635. The results are shown in Table 4.

## &lt;Mixture&gt;

Polyvinyl chloride resin (Geon 103EP)	100 parts by weight
Dioctyl phthalate (DOP)	40
Phosphate halide (Table 4)	10
Barium nonyl phenolate	0.5
Zinc octoate	0.3
Trisnonylphenyl phosphate	0.1
Dibenzoyl methane	0.01

Table 4

No.	Phosphate halide	Initial discoloration	Heat stability	Combustibility
Comparative example 4-1	DOP	Good	105	Combusted
Working examples 4-1	Tris(2-chloroethyl)phosphate	Good	105	Self-extinguished
4-2	Tris(chloropropyl)phosphate	Good	120	Self-extinguished
4-3	Tris(2,3-dibromopropyl)phosphate	Good	105	Self-extinguished
4-4	Tris(dichloropropyl)phosphate	Good	120	Self-extinguished
4-5	Bis(chloropropyl)monophenyl phosphate	Good	120	Self-extinguished